

Greenhouse Gas Emissions from Fossil Fuel Use and
Technical Approaches to their Control

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Introduction

Radiative trapping or forcing by so called greenhouse gases in the atmosphere causes the mean surface temperature of Earth to be 33 K higher than it would be in their absence. While the greenhouse effect is thus necessary for life as we know it, there is concern that additional unwanted warming may occur as a result of increasing concentrations of greenhouse gases. Analysis of air bubbles trapped in glacial ice shows that starting roughly with the onset of industrialization in the late 18th and early 19th centuries, the concentration of all greenhouse gases found in nature began to increase¹. Through 1991 the concentration of CO₂, the gas causing the greatest amount of radiative forcing, had increased by over 25% from its preindustrial value. The other main greenhouse gases that occur in nature, CH₄ and N₂O, exhibit similar increases since the early 1800s. While the timing and extent of global warming that may result from increased concentrations of greenhouse gases is uncertain, it is prudent to understand the main sources of anthropogenic greenhouse gases and the conditions governing their release. All three of the principal greenhouse gases existing in nature are released in the course of fossil fuel use, and for all three, fossil fuel emissions are a significant component of total anthropogenic emissions¹. In this paper the emissions of CO₂, CH₄, and N₂O in the contemporary United States due to use of the fossil fuels natural gas, oil, and coal are presented. Details of the calculations will be given in a subsequent publication². The relative importance of each of these gases for radiative forcing is shown. Some technologies under development that can reduce emissions of these trace gases per unit of useful heat or work obtained are discussed.

The amount of radiant energy a mole of a particular greenhouse gas absorbs during its atmospheric lifetime depends on its lifetime and its absorption strength, integrated over all active wavelength bands. An index called the global warming potential, or GWP, has been developed to compare the lifetime effect of one mole (or one kg) of a particular greenhouse gas to that of a similar amount of CO₂. The GWP for trace gas *i* is defined³:

$$GWP_i = \frac{a_i \int_0^T c_i(t) dt}{a \int_0^T c(t) dt} \quad (1)$$

Here a_i is an absorption coefficient, c_i is concentration in mass or molar units, and t is time. Unsubscripted values refer to CO₂. The average atmospheric

lifetimes of the trace gases are as follows: CO₂, 100-120 y; CH₄, 10-12 y; N₂O, 150-180 y. When eq. 1 is integrated over a time T of 100 y, the computed GWPs for CH₄ and N₂O are 7.6 and 290, respectively, expressed on a molar basis³.

1. Emissions of CO₂

For complete combustion of any fuel, the specific carbon emission, or carbon emission factor, defined as g C as CO₂ per MJ heat released, is determined by its composition and heating value. It is preferable to use the lower heating value (LHV) for the calculation, since in most applications water produced in combustion leaves the process as a vapor. A correlation of heating value as a function of elemental composition of a fuel shows how the carbon emission factor depends on fuel composition⁴. Although developed specifically for coal, it describes oil and natural gas as well.

$$\Delta H_L = 341 C + 1102 H + 68.4 S - 15.3 A - 119 (O + N) \quad (2)$$

Here, C, H, S, and (O+N) are the percentage of elements and A is ash or other inert by weight on a moisture free basis. The heating value is in J/g (LHV). It is seen that on a weight basis, hydrogen is the component with the largest energy content. Carbon is next largest, but it figures in the numerator as well as denominator of the expression for carbon emission factor. Oxygen and nitrogen have negative values because their presence in a fuel causes it to be partially oxidized. For coal, the combined effect of C, H, and O dependence causes the carbon emission factor to go through a minimum with the rank of hv bituminous.

Natural Gas

Consumption of natural gas in the U.S. in 1989 was 481 billion m³ (20.3 EJ (HHV)). To convert this figure into CO₂ emissions requires information on composition of the gas at the wellhead and also at the burner tip. The difference between the two compositions is due to processing of the natural gas before transmission by pipeline. In processing, undesirable components including CO₂ are removed, the CO₂ being vented. The CO₂ produced due to flaring at the well must also be counted. Equations are developed for a carbon emission factor for natural gas that takes into account CO₂ emissions from venting and flaring. Application to domestically produced natural gas in 1989 yields an emission factor of 15.17 gC/MJ (LHV). Imported gas is analyzed similarly. Total CO₂ emissions in 1989 from consumption of natural gas is estimated to be 278.2 M tonne C.

Oil

In 1989, total crude oil processed in the U.S. was about 13.5 million barrels per day with the balance of liquid fuel consumption comprising natural gas liquids and imported refined products. A small fraction of petroleum (about 5 %) was exported. Total oil-based energy consumed in the U.S. was about 36 EJ. Emission factors for imported refined products and for crude oil (combined domestic production and imports) were computed and used to calculate carbon emissions by product class. The carbon emission factor for crude oil is 19.96 gC/MJ (LHV). The factor for products falls in the range 18.4-21.5 gC/MJ (LHV) depending on fuel composition. Total estimated CO₂ emissions from petroleum consumption in the U.S. during 1989 was 625.1 M tonne C.

Coal

The carbon content of coal per unit of heat content is found to vary with coal rank. Equation 2 has been used with composition data for U.S. coals to compute carbon emission factors by rank. The emission factor for lignite, the highest for all coal ranks, is 26.9 gC/MJ (LHV), about 8 % higher than for hVA bituminous, the lowest at 24.6 gC/MJ (LHV). The emission factors have been used with U.S. coal consumption by rank in 1989 to compute carbon emissions. In 1989 total U.S. coal production was 890 M tonnes, and coal consumption, expressed as energy, was 19.69 EJ (HHV). The largest carbon emission was from the bituminous grades, which represented 70% of total emissions, but supplied 74% of the total energy. Overall carbon emissions are calculated as 490.5 M tonnes C, which agrees well with the estimate of Marland⁵, which was prepared without use of rank-specific carbon emission factors.

2. Emissions of CH₄

Methane emissions result from the production and distribution of oil and gas, and from the mining of coal. The losses from oil and gas operations are considered in three categories.

- o Venting and flaring of methane occurring at the well head in the production of natural gas and oil.
- o Production, gathering, and processing losses.
- o Transmission and distribution losses.

The following discussion provides estimates of methane emissions from fossil fuel use in the U.S. during 1989.

Venting/Flaring Emissions in Oil/Gas Production

Venting and flaring of methane during production and processing of oil and gas is due to purposeful venting, routine maintenance, and system upsets and mishaps. There are insufficient data to apportion these emissions to oil or gas and to determine their composition. We estimate the fraction of methane in venting/flaring emissions to be 20%. Based on total reported venting and flaring emissions for the U.S. in 1989, emissions of methane are estimated to be 0.41 Tg.

Production Losses

Leakage of methane occurs from field production and processing operations. These are primarily from fugitive emissions such as leaks from valves, pipes, compressors, and other equipment during normal operation of gas gathering, separation from condensate/oil, reinjection, and processing. The leakage rate varies between oil and gas wells and between offshore and onshore operations, due to significantly different processing equipment and conditions. Production losses of CH₄ are calculated to be 0.44 Tg.

Transmission/Distribution Losses

Natural gas is transported via high pressure pipeline throughout the U.S. with

local distribution networks consisting of low pressure delivery systems. Including low pressure distribution lines, the total length of pipe is estimated to be over 1.5 million miles. Several key components are subject to leakage: compressor shaft seals, valve stem packing, relief valve escapes, and flanged joints. Methane emissions from transmission/distribution losses is estimated as 1.77 Tg.

In addition to the three categories of CH_4 losses tabulated above, a relatively small amount is added for incomplete methane combustion. Allowing 0.5 g CH_4 per GJ adds an additional 0.009 Tg to 1989 emissions in the U.S. Total estimated CH_4 losses due to oil and gas operations thus sum to 2.63 Tg in 1989. By use of the GWP for CH_4 developed above, the importance of these losses for radiative forcing relative to the CO_2 emitted in the combustion of the oil and gas consumed in the U.S. in 1989 can be computed. The radiative forcing due to CH_4 emissions is 1.7% of that due to CO_2 from natural gas and oil combustion.

Methane Emissions as a Result of Coal Mining Activities

Correlations have been developed to relate CH_4 emissions to coal production by use of an overall emission factor. Such a factor, in m^3/tonne , expresses the ratio of total methane emissions to total coal production. Emission factors depend on in-place coal methane content. However, in addition to the gas contained in coal that is removed, methane may be released from adjacent gas-bearing strata and exposed but unmined coal during and after mining. Emissions from these sources are also included in computing an overall emission factor.

Overall emission factors have been developed by several workers in recent years and used to estimate CH_4 emissions from coal mining^{6,7,8,9}. The emission factors fall in the range 6.02-11.77 m^3/tonne . Smith and Ruether calculate the emission factor as 7.74 m^3/tonne and estimate total CH_4 emissions in 1989 as 5.0 Tg⁹. The greatest fraction, 4.2 Tg, was due to deep mining operations. The importance of these emissions for radiative forcing relative to those of the CO_2 produced in coal combustion can be estimated as above. In 1989, U.S. production of deep mined coal was 357 million tonnes, and the radiative forcing of CH_4 emissions from deep mines was equivalent to about 9% of the forcing due to combustion of deep mined coal.

3. Emissions of N_2O

Production of N_2O in the course of fossil fuel use occurs via direct emissions and also via an indirect route from emissions of NO and NO_2 , collectively called NO_x . In the atmosphere, NO_x are oxidized and return to the earth as acid precipitation. It is known that soil-bearing microbes reduce nitrates applied as fertilizer, resulting in N_2O emissions to the atmosphere. This mechanism presumably applies to nitrates originating as acid precipitation as well¹³. The extent of conversion of nitrate to N_2O by soil microbes is not well known, but Robertson estimated N_2O formation to be 1% of total fertilizer nitrogen, nitrate and ammonia¹⁰. If 1% of N as NO_x is converted by microbes to N_2O , this is an important indirect route in fossil fuel combustion to N_2O .

About 30% of fossil fuels consumption in the U.S. is for the transportation sector with the remainder used in stationary sources ranging from residential heating to electric utility boilers. The N_2O emissions from the largest stationary sources, utility boilers, have been most studied. Early estimates of

N₂O emissions from stationary sources were erroneously high due to an artifact of the analysis procedure¹¹. More recent results are given in Table 1 where both NO_x and N₂O emissions are shown for a number of utility boilers firing all three fossil fuels¹². It is seen that except for the circulating fluidized bed combustor, the greater contribution to N₂O emissions is due to the indirect route if the assumed 1% conversion of NO_x to N₂O is correct. Because per molecule N₂O has two atoms of N while NO_x has one, a 1% conversion of NO_x to N₂O is equivalent to a direct N₂O emission of 0.5% of NO_x. The right hand side of Table 1 shows the effect on NO_x emissions of several technologies being developed for their control. The effect of these technologies on direct N₂O emissions is poorly understood at present.

The transportation sector produced 44% of total NO_x emissions from fossil fuel use in 1989. It is thus an important producer of N₂O via the indirect route. It is also responsible for significant direct emissions of N₂O. These emissions vary with vehicle type and whether a catalytic converter is employed. (Catalytic converters increase N₂O emissions 10-fold¹⁰.) On an energy basis, direct N₂O emissions from vehicles are substantially higher in general than those from high temperature stationary boilers. Due in large part to the unknown extent of indirect production of N₂O from NO_x, estimates of N₂O production from fossil fuel use are highly uncertain. For instance, two recent estimates for global emissions were 0.3 Tg and 5.0 Tg^{13,14}.

4. Technologies to Reduce Greenhouse Gas Emissions

Carbon Dioxide

For a given fossil fuel, reduction of CO₂ emissions per unit of useful heat or work output requires increased energy conversion efficiency. Natural gas consumption is expected to rise in the U.S. in the 1990s primarily for increased power generation using gas turbines. The efficiency for power generation via simple cycle, e.g., gas turbine, for current typical units is 25-30% and for combined cycle units, 35-40%. With recent improvements, cycle efficiency has improved considerably to 35.5% for simple cycles and 52.5% for combined cycle. Further advances now on the horizon may increase combined cycle efficiencies to the range of 55-60%. Synthesis gas, the fuel for molten carbonate and solid oxide fuel cells, can be made by reforming natural gas. These fuel cells alone yield an efficiency in the range 45-50%, and when combined with a thermal bottoming cycle may give an overall efficiency of 60-65%.

There are similarly both short term and longer term efficiency improvements for coal-fired power cycles. In the current population of coal-fired power plants, 22% of the plants operate with an efficiency of less than 31%. Only about 10% have an efficiency of greater than 36%. Typical operating conditions for current pulverized coal-fired boilers are 2400 psig steam with 1000 °F superheat and reheat. Commercially proven technology is available with steam operating conditions in the range 3500-4500 psig with main and reheat temperatures in the range 1050-1100 °F, which yield efficiencies of about 40%. This is close to the efficiency expected for pressurized fluidized bed combustors, in an advanced state of development. In the medium term, new or revisited power cycles (Kalina cycle, employing water/ammonia working fluid; indirectly heated gas turbine combined cycle) are expected to yield efficiencies of 45-50%. Other high efficiency approaches are combined cycle gasification/fuel cell, and combined cycle gasification/gas turbines. Longer term, magnetohydrodynamics (MHD) shows

promise of an efficiency in the neighborhood of 60%.

Methane

The main contributor to CH_4 emissions from oil and gas operations is the transmission and distribution system, which accounts for two-thirds of the total. A more rigorous maintenance schedule and accelerated replacement of aging pipelines would help reduce these emissions. New transmission systems are estimated to leak only one-fourth as much as older systems, on average. One possible pipeline replacement program would result in about 0.6 Tg reduction in annual emissions after 10 years. There also appears to be scope for reduction of CH_4 currently vented. At a minimum, if this methane is flared (burned) before release, its effect on radiative forcing is reduced by a factor of about 7. Where venting or flaring is currently practiced on a regular schedule, it may be possible to install transportable electrical generating equipment employing gas turbine or internal combustion engines (see below). This would have the double benefit of converting CH_4 to CO_2 and generating usable power with no additional use of fossil fuel.

Much of the estimated 5.0 Tg CH_4 emitted from U.S. coal mines in 1989 has the potential for useful recovery. Components that are potentially useful are ventilation gas (2.8 Tg), typically 0.3-1.0% CH_4 , gas produced by degasification systems (1.3 Tg), typically 25-95% CH_4 , and emissions from abandoned deep mines (0.5 Tg), of variable composition. Ventilation gas is too dilute to support combustion by itself, but if used as the source of combustion air with another high concentration CH_4 source, it could contribute about 15% of the fuel to a gas turbine. Degasification gas can serve as the sole fuel source for power generation by internal combustion engines, as is presently being demonstrated¹⁵. Transportable generator modules are being developed that can be taken to remote mine sites to generate power used at the mine and potentially also for export to a power grid. If gas is purposely withdrawn from abandoned deep mines, it also could serve as the fuel for such a generator module.

Nitrous Oxide

As discussed above, both the transportation sector and stationary sources are significant sources of N_2O . Improvement of vehicle mileage would obviously reduce N_2O emissions from the transportation sector. Redesign of catalytic converters should be possible to reduce direct N_2O emissions. These emissions were not a consideration in the original design. Development of electric vehicles would also reduce N_2O emissions, since on an energy basis, stationary sources needed to generate the electricity to charge vehicle batteries, emit less N_2O and NO_x than do vehicles.

For stationary sources, the Clean Air Act Amendments of 1990 will require a 2 million ton per year reduction in NO_x emissions. A number of technologies for NO_x control, some of them listed in Table 1, are being demonstrated at commercial scale through the U.S. DOE Clean Coal Technology program.

REFERENCES

- (1) Bolin, B. in *The Greenhouse Effect, Climatic Change, and Ecosystems-SCOPE 29* (ed Bolin, B., Doos, B.R., & Jager, J.), Wiley, Chitester, 1986; pp 93-

- (2) Ruether, J.A.; Smith, D.N.; Rao, S.N. (in preparation).
- (3) Shine, K.P.; Derwent, R.G.; Wuebbles, D.J., & Morcrette, J.-J. in *Climate Change: The IPCC Scientific Assessment* (eds Houghton, J.T., Jenkins, G.J., & Ephraums, J.J.), Cambridge University Press, Cambridge, 1990, pp 41-68.
- (4) Institute of Gas Technology *Preparation of Coal Conversion Systems Technical Data Book*; Quarterly Report for August-October 31, 1977, U.S. Department of Energy FE-2286-24, 1978.
- (5) Marland, G. *Carbon Dioxide Emissions From Fossil Fuels: A Procedure For Estimation And Results For 1950-1981* Oak Ridge Associated Universities Report TR003, prepared for Department of Energy DOE/NBB-0036, Washington, DC, 1983.
- (6) Barns, D.W.; Edmonds, J.A. *An Evaluation of the Relationship Between the Production and Use of Energy and Atmospheric Methane Emissions* Pacific Northwest Laboratory, prepared for the Department of Energy DOE/NBB-0088P, Washington, DC, 1990.
- (7) Science Applications, Inc. *Overview of Unconventional Natural Gas Research and Development Activities* McLean, Virginia, NTIS, PB 80-227986, 1980.
- (8) Boyer, C.M.; Kelafant, V.A.; Kuuskraa, V.A.; Manger, K.C.; Kruger, D. *Methane Emissions from Coal Mining: Issues and Opportunities for Reduction*. Prepared by ICF Resources Inc. under contract to U.S. EPA, Washington, DC, 1990.
- (9) Smith, D.N.; Ruether, J.A. (in preparation).
- (10) Robertson, K. *Ambio* 1991, 20, 3, 151-154.
- (11) Muzio, L.J.; Montgomery, T.A.; Samuelson, G.S.; Kramlich, J.C.; Lyon, R.K.; Kokkinos, A. *Formation and Measurement of N₂O in Combustion Systems*. Comb. Institute Symposium. Orleans, France, 1990.
- (12) Kokkinos, A.; Cichanowicz, J.E.; Hall, R.E.; Sodman, C.B. *J. Air Waste Manage. Assoc.* 1991, 41, 9, 1252-1259.
- (13) Levine, J.S. *The Global Atmospheric Budget of Nitrous Oxide*, in Proceedings: 1991 Joint Symposium on Stationary Combustion NO_x Control, NTIS, Springfield, VA.
- (14) Prinn, R.; Cunnold, D.; Rasmussen, R.; Simmonds, P.; Alyea, F.; Crawford, A.; Fraser, P.; Rosen, R. *J. Geophysical Res.* 1990, 95, D11, 18:365-18:385.
- (15) Soot, P. *Coal Mine Natural Gas Power Generation*, Phase I Final Report, U.S. DOE Contract DE-AC02-89ER-80796.A00, 1990.

TABLE 1 NO _x AND N ₂ O EMISSIONS FROM UTILITY AND INDUSTRIAL COMBUSTION											
Combustor Type	MWe	Fuel	Uncontrolled Emissions, (ppm)			Control Technology ¹	Controlled Emissions, (ppm)				
			NO _x		N ₂ O		NO _x	N ₂ O		Total	
			Direct	Indirect				Direct*	Indirect		
1. Tangential	160	Coal	1	2.5	3	OFA	223	@	1.1		
2. Tangential	165	Coal	1	2.0	6	LNCf	292	@	1.5		
3. Wall Fired	500	Coal	2	4.8	6	AOFA	730	@	3.7		
4. Wall Fired	800	Coal	1	4.0	5	GRB	380	@	1.8		
5. Wall Fired	110	Coal	1	3.7	3	LNB	360	@	0.4		
6. Wall Fired	185	Coal	2	0.6	2	GRB	80	@	0.4		
7. Wall Fired	N/A	Coal	2	1.3	84	-	-	-	-		
8. CFBC	N/A	Coke	1	0.4	16	-	-	-	-		
9. Fluid Bed Catalytic Cracker	75	Coal	14	2.2		SNCR	120	33	0.6	11	
10. Tangential	110	Coal	200*	1	1.0	SNCR	60	10.6	0.3	24	
11. Tangential	110	Oil	300*	1	1.5	SCR	117	23	0.6		
12. Wall Fired	110	Oil	291	1	1.5	SNCR	117	23	0.6		

* Includes direct emissions increase due to post combustion NO_x control.
 * Employed combustion zone NO_x control
 @ Not measured
 1. OFA (over-fired air)
 2. LNCf (low-NO_x combustor)
 3. SNCR (selective non-catalytic reduction of NO_x)
 4. GRB (gas gas-reburning)
 5. SCR (selective catalytic reduction of NO_x)
 6. AOFA (advanced over-fire air)
 7. LNB (low-NO_x burner)

LNB (low-NO_x burner)

AOFA (advanced over-fire air)

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